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Published in:
Synthetic Metals

DOI:
10.1016/S0379-6779(00)00682-2

Publication date:
2001

ELSEVIER

Synthetic Metals 121 (2001) 1621–1624

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Charge transport in polymer light-emitting diodes

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Abstract

The transport of electrons and holes in poly(dialkoxy-p-phenylene vinylene) (PPV) has been investigated using temperature dependent current density-voltage characteristics and admittance spectroscopy. From admittance spectroscopy, both the electron and hole mobility of PPV can be obtained from a single polymer light-emitting diode (PLED). These experiments reveal that at room temperature the electron transport is strongly reduced with regard to the hole transport. Due to the smaller activation energy of the electron transport the difference between electron and hole transport in PPV diminshes with decreasing temperature.

Keywords: Transport measurements, poly(phenylene vinylene) and derivatives, light sources

1. Introduction

In the 1950s and early 1960s the studies on organic conductors focused on the understanding of the electric and optical properties of anthracene molecules in the crystalline state. Mette and Pick (1953) [1] reported very high resistivities in the neighborhood of 10^{14} Ω cm, which makes anthracene essentially an insulator. From a pulsed photoconductivity technique Kepler (1960) [2] determined electron and hole mobilities of typically 1 cm^2/Vs for anthracene crystals. Furthermore, Pope et al. (1963) [3] reported the observation of electroluminescence in anthracene single crystals. At the end of the 1960s the focus of the investigations to organic semiconductors moved from anthracene single crystals to photoconducting polymers such as poly(N-vinylcarbozole) (PVK). It had been shown by Hoegl (1965) [4] that the photoconductivity of PVK could significantly be enhanced by addition of electron acceptors. This increased photoconductivity, the fact that PVK can be deposited as a thin film and the favorable mechanical properties of these molecularly doped polymers made this class of materials suited for xerographic applications. Using time-of-flight (TOF) measurements it has been demonstrated [5] that the mobility of photoexcited holes in PVK exhibits a dependence on the electric field according to

$$\mu(E) = \mu_0 \exp\gamma\sqrt{E} \qquad (1)$$

with E the applied electric field. Gill [6] proposed an empirical law for the hole mobility in this class of materials according to

$$\mu_p(E) = \mu_0 \exp\left[-\frac{\Delta}{k_B T} + B\left(\frac{1}{k_B T} - \frac{1}{k_B T_0}\right)\sqrt{E}\right] \qquad (2).$$

This field- and temperature dependence of the mobility has been observed in a large number of disordered molecular materials [7]. The activation energy Δ ranges from 0.4-0.6 eV, B is typically 3×10^{-5} $eV(m/V)^{1/2}$, and T_0 ranges from 400-600 K. This universal behavior of the mobility for a large number of different materials suggests the existence of a common microscopic charge transport mechanism for disordered conductors. In 1977 it was demonstrated [8] that the conduction of the conjugated polymer polyacetylene could be continuously varied over eleven orders of magnitude when doped with arsenic pentafluoride. The demonstration of field-effect transistors made from polythiophene [9] and electroluminescence in PPV based PLEDs [10] strongly enhanced the attention for conjugated polymers. A major question with regard to the operation of PLEDs is whether the charge carrier mobility of conjugated polymers also obeys the universal behavior [Eq. (2)], similar to molecularly doped polymers and organic glasses as observed in the 1970s and 1980s using TOF experiments.

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PII: S0379-6779(00)00682-2

2. Hole transport in PPV

The devices under investigation consist of a single polymer layer sandwiched between two electrodes on top of a glass substrate. As a bottom electrode patterned indium-tin-oxide (ITO) has been used, on top of which the soluble PPV is spin coated. The work function of ITO is expected to be close to the valence band of the PPV, which is favorable for the injection of holes. As a top electrode evaporated Au is used. In forward bias the ITO electrode serves as the anode and Au as the cathode. Since the work function of Au is also close to the valence band of PPV electron injection is prevented under forward bias and only holes will flow into the PPV. From current density vs. voltage (*J-V*) characteristics it has been demonstrated [11] that the hole current in these PPV hole-only devices is space-charge limited (SCLC). The observation of a SCLC implies that the ITO contact is Ohmic and furthermore, it enables the possibility to determine the charge carrier mobility directly from the *J-V* characteristics. At higher fields the *J-V* characteristics are described by taking into account the field-dependence of the mobility (Eq. [2]) [12]. In Fig. 1 the *J-V* characteristics of a hole-only device are shown at T=195 K and 300 K.

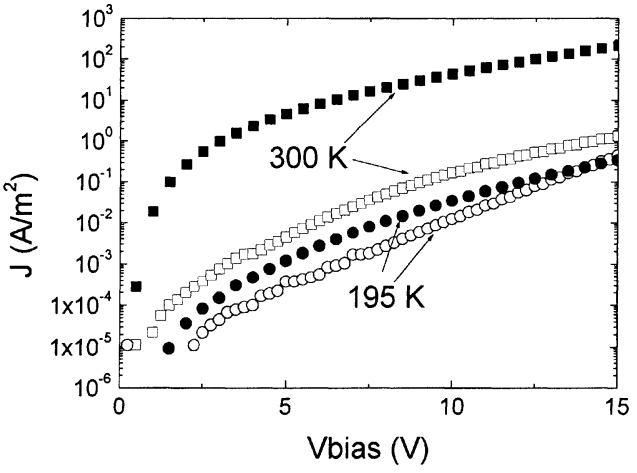

Fig.1. Experimental *J-V* characteristics of a ITO/PPV/Au hole-only device (closed symbols) and a Ca/PPV/Ca electron-only device (open symbols) at T=195 and 300 K. The device thickness amounts to *L*=240 nm.

The experimental hole current is well described [12] by the 'universal' mobility [Eq (2)] using the following parameters: Δ=0.48 eV, B=2.9×10^{-5} eV(m/V)$^{1/2}$, T_0=600 K and μ_0=3.5×10^{-3} m^2/vs. For PVK B=2.7×10^{-5} eV(m/V)$^{1/2}$ and T_0=520-660 K was reported [6], which is in close agreement with the values found for the conjugated polymer PPV. This suggests that the conduction mechanism in conjugated polymers are similar to molecularly doped systems, where highly localized carriers are transported by thermally assisted intermolecular hopping. In a conjugated polymer which contains disorder in the form of kinks, cross-links and impurities, the conduction may strongly depend on hopping between conjugated parts of the chain and between conjugated parts of different chains.

For a further investigation of the dynamics of the charge transport in PLEDs the admittance spectroscopy technique can be applied [13]. Previous alternating current (ac) studies performed on PLED's have been interpreted in terms of equivalent RC-circuit models. A possible frequency dependence of the circuit components had not been taken into account in the analysis of the ac measurements. The observed bias dependence of the capacitance has been interpreted in terms of charge trapping [14] and Schottky behavior [15]. In Fig. 2 the ac response of the capacitance, defined as C=Im(Y/ω), with Y the complex admittance i_{ac}/v_{ac}, of an ITO/PPV/Cu hole only device is shown for different bias voltages. The capacitance curves are off-set by 0.5 nF for clarity.

It appears that the capacitance *C* exhibits a distinct frequency dependence; at low frequencies C decreases and the frequency at which this decrease stops shifts to higher

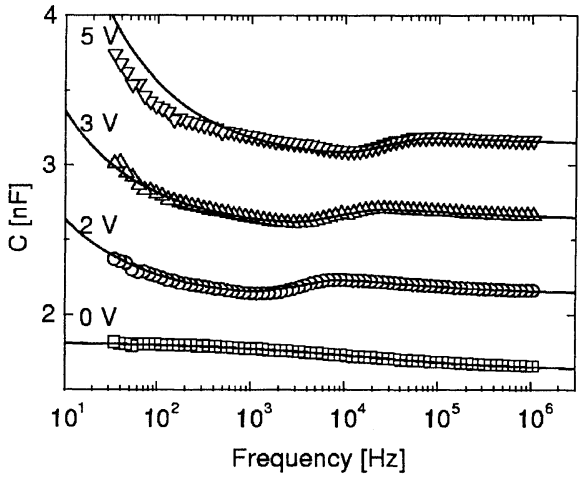

Fig. 2. Frequency dependent capacitance *C* of a Au/PPV/Cu hole only device at various applied voltages. The capacitance traces are off-set by 0.5 nF for clarity.

frequencies with increasing voltage. For the interpretation of these results it is important to realize that, since the device is space-charge limited, v_{ac} directly modulates the number of charge carriers in the device. However, the time-scale for the built-up of charge carriers is given by the transit time τ_t of the injected holes. At low frequencies $\omega<\tau_t^{-1}$ the build up of space charge is fast enough to follow the modulation in v_{ac}. Due to the finite τ_t the corresponding current lags behind the v_{ac} and this results in an additional inductive (negative) contribution to the capacitance. For high frequencies $\omega>\tau_t^{-1}$ the space charge

can not be redistributed in a period of the applied voltage v_{ac} and the measured capacitance equals the geometrical value, $C_0=\varepsilon A/L$. These contributions to C are clearly visualized when the negative differential susceptance $-\Delta B = -\omega(C-C_0)$ is plotted, as shown in Fig. 3.

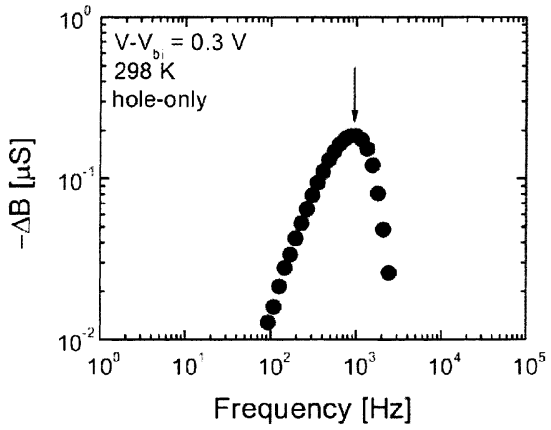

Fig. 3. Negative differential susceptance $-\Delta B=-\omega(C-C_0)$ of a Au/PPV/Cu hole-only device at T=298 K.

The frequency at which the maximum of the relaxation peak appears, ω_{max}, is directly related to the transit time τ_t according to $\omega_{max}=3.4\times\tau_t^{-1}$. From the transit time the DC hole mobility can directly be obtained. The magnitude and field dependence of the DC mobility is in excellent agreement with the result from our earlier DC (J-V) measurements [13].

3. Electron transport in PPV

The transport properties of electrons have been investigated using an electron-only device consisting of a PPV layer sandwiched between two Ca electrodes, which have a work function close to the conduction band of PPV. In Fig.1 the J-V characteristics of electron-only devices with thickness L=240 nm are shown together with the J-V characteristic of a hole-only device (L=240 nm) at T=195 and 300 K. At T=300 K the electron current is smaller than the hole current, especially at low bias where the difference amounts to three orders of magnitude. Such a strongly reduced electron conduction has also been observed in TOF measurements in which deep trapping products for electrons and holes had been determined for PPV [16]. Furthermore, the electron current shows a stronger field-dependence with regard to the hole current. Initially, the combination of a reduced electron current and stronger field dependence at 300 K has been interpreted in terms of an exponential distribution of traps [11].

However, the observed temperature dependence of the electron current, as shown in Fig.1, can not be explained by such a trap model. Additional trap levels will give rise to a stronger dependence on temperature, which is in contrast with the experiments. The exponential trap distribution has also been used to describe the J-V characteristics of organic LEDs based on metal chelate complexes [17]. However, data on metal chelate as well as polymer based devices could also be explained by a field- and temperature mobility without introducing traps [18].

It should be noted that an exponential trap model is only valid for traps which are in thermal equilibrium with the conduction band. For charge carriers hopping in a distribution of localized states, especially with long escape times from deeper states, the concept of thermal equilibrium is highly questionable [19]. Furthermore, due to the strong dependence of the hopping probability on electric field, it is expected that electrons which are trapped in deep states will be released at high electric fields. Thus the exponential trap model used initially [11], which does not include field-assisted escape, is probably too simple in order to quantitatively explain the field- and temperature dependence of the electron current. Another striking result of Fig.1 is that at T=195 K the difference between the electron and the (trap-free) hole current nearly disappears, which has also recently been observed by Bozano et al. [20]. In terms of a trapping model this would indicate that the traps, which strongly reduce the electron current at T=300 K, would loose their activity at lower temperatures.

In order to further investigate the charge transport we have applied admittance spectroscopy to ITO/PPV/Ca PLEDs, in which both holes and electrons are injected. In Fig. 4 the differential susceptance $-\Delta B=-\omega(C-C_0)$ is plotted for such a device with a thickness L=150 nm.

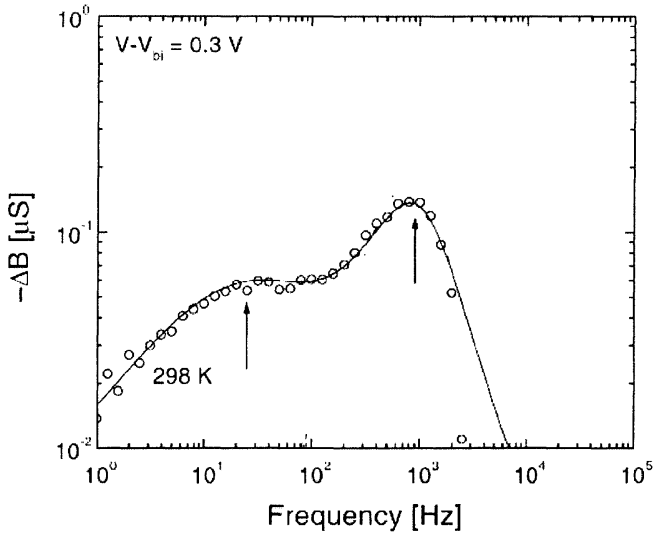

Fig. 4. Negative differential susceptance $-\Delta B=-\omega(C-C_0)$ of a PLED at T=300 K., which exhibits two relaxation peaks due to the different electron and hole transit times.

In the PLED now two relaxation peaks are observed, with one peak at the identical position as compared to the hole only device. The low frequency peak then applies to the transit time of the electrons in the device. As a result, by using admittance spectroscopy we are able to simultaneously measure the electron and hole mobility in a single PLED by separating them in the frequency domain. In fig. 5 the mobility at zero field is shown for both electrons and holes.

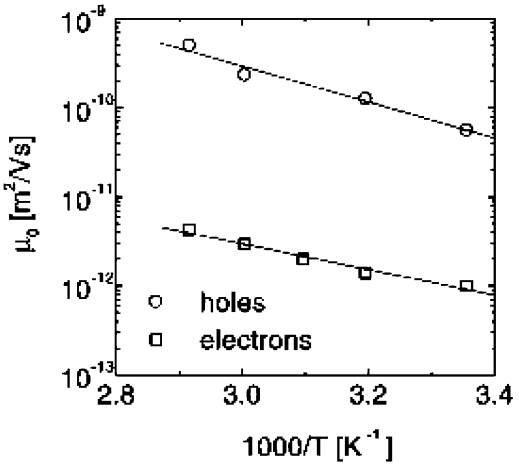

Fig. 5. Arrhenius plot of the zero-field mobility of electrons and holes versus T as obtained from the admittance measurements. The activation energy for electrons and holes amounts to 0.29 eV and 0.42 eV respectively (lines).

Applying Eq. (2) to the obtained mobilities gives for holes Δ=0.42 eV, B=3.1×10^{-5} eV(m/V)$^{1/2}$, T_0=520 K and μ_0=3.1×10^{-3} m^2/vs, which is in good agreement with the values as obtained from the J-V characteristics [12]. For electrons we find: Δ=0.29 eV, B=3.1×10^{-5} eV(m/V)$^{1/2}$, T_0=900 K and μ_0=6.5×10^{-8} m^2/vs, which is in excellent agreement with the parameters as obtained by Bozano et al. from J-V measurements on MEH-PPV [20].

The microscopic origin of the trap-free hole mobility can be explained by hopping transport in a (correlated) Gaussian disorder model [19,21]. It has been demonstrated [22] that the hole mobility in our PPV is characterized by a disorder band width σ=112 meV. Applying the same analysis to electrons, the weaker temperature dependence of the observed electron mobility would result in σ=95 meV. Such an apparent reduction of the energetic disorder is expected to enhance the charge transport, and is in contrast with the fact that the electron mobility is strongly reduced with regard to the hole mobility. Recent simulations of hopping transport in a disordered system including traps indicate that the presence of traps induce an additional field dependence of the mobility [22], as is experimentally observed for electrons. As a result, the relatively low electron mobility and its strong field dependence are indications for the presence of traps. The reduced temperature dependence, however, which is in contrast to the predictions of classical trap models, has not been addressed so far in these simulations and is a subject of further research.

In conclusion, the conduction of holes in a film of the conjugated polymer PPV is governed by a combination of a field-dependent mobility and space charge effects. The field-dependent mobility originates from charge carriers hopping in a system with energetic disorder. At room temperature, the electron transport is strongly reduced with regard to the hole transport. The reduced electron mobility combined with an enhanced field dependence might arise from trapping effects, its microscopic origin has not been resolved so far.

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